Poly(lactic acid) and Osage Orange wood fiber composites for agricultural mulch films[☆]

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ABSTRACT

Osage Orange wood (OO) was combined with poly(lactic acid) (PLA) to form a polymer composite intended for use as an agricultural mulch film. The PLA–OO mechanical properties were comparable to existing mulch film products and had the advantage of being completely biodegradable through a single growing season. PLA–OO composites were evaluated for mechanical properties in both dry and wet conditions. The availability of its organic components useful for release into the environment was determined to be significantly higher than native OO before thermomechanical treatment. PLA–OO mulch films will provide a weed barrier and control soil erosion, as well as allowing the controlled release of the OO phytochemical components for additional protection.

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1. Introduction

Crop protection is a critical issue in agriculture. Crop protection measures include climate control, mitigating environmental conditions, and improving growth parameters (Briassoulis et al., 2004; Kyrikou and Briassoulis, 2007; Kapanen et al., 2008). Non-degradable plastics, usually low-density polyethylene, have been used increasingly by farmers to protect crops (Kyrikou and Briassoulis, 2007). Agricultural mulch films have been shown to control soil temperature, limit soil erosion, reduce water and pesticide consumption, deliver nutrients, and suppress weeds. The lifetime of an agricultural mulch film varies considerably (e.g., months to years) depending on its application and the environmental conditions (Kyrikou and Briassoulis, 2007). Normally, for tree orchards or vineyards, the plastic mulch film is relatively thick and has a lifetime of years until it loses its effectiveness. In contrast, for vegetable fields, the film is thinner and usually lasts a single growing season. In any case, at some point, the plastic films must be removed from the fields. The recovery of non-degradable plastic mulch films is labor-intensive, economically prohibitive and frequently unattractive (Chiellini and Salaro, 2002). Many mulch films remain littered in the landscape or burned onsite. Even if recovery and disposal were mandated, the waste must be treated as a special hazard due to biological contamination or impregnation of fertilizers, pesticides or fungicides employed to actively control plant growth, regulation and weed control (Kapanen et al., 2008). Sustainable agricultural practices demand bio-based biodegradable plastics to replace petroleum-based non-degradable plastics for use as agricultural mulch films. Biodegradable plastics, such as poly(lactic acid) or PLA, are good alternatives to petroleum-based plastics (Bogaert and Coszach, 2000). PLA is a hydrophobic polymer prepared from renewable agriculture-based feed stocks (usually corn starch or dairy whey) which is fermented to lactic acid and then polymerized. PLA has mechanical properties comparable to petroleum-based plastics and can be extruded and injection molded, but is currently more expensive (Garlotta, 2001). Under normal soil or compost conditions, PLA decomposes into water, carbon dioxide and humus (Drumright et al., 2000; Ghorpade et al., 2001; Tuominen et al., 2002). Sarasa et al. (2009) showed that neat PLA and corn meal filled (10%, w/w) PLA degraded approximately 60% and 80%, respectively, after 90 days with aerobic digestion at 60 °C at compost conditions (Sarasa et al., 2009). PLA is non-toxic and in some cases can promote plant growth (Kinnersley et al., 1990). If a shorter lifecycle is necessary, partially degraded

PLA can be plowed into the soil. Other bio-based polymers have been used for agricultural mulch films such as starch (Halley et al., 2001), starch and polycaprolactone (PCL) (Kapanen et al., 2008), and starch–poly(vinyl alcohol) (PVOH) (Chandra and Rustgi, 1998). PCL and PVOH are both petroleum-based polymers.

Maclura pomifera, commonly called Osage Orange (OO), is native to the United States, was planted as a wind break along fence lines, and is widely recognized by its giant green fruit (hedge or horse apple) (Smith and Perino, 1981). OO grows relatively fast, in diverse environments, and is considered appropriate for remediation of marginal or disturbed sites such as mines (Barnett and Burton, 1997). Use of OO for hedgerows helped delineate farm boundaries in the western United States in the 1800s and more recently was also suggested as a landscaping tree (Baudry et al., 2000). OO is considered the hardest and most dense wood relative to other trees (Clopton and Roberts, 1949). Much work has been done on the characterization of pigments, antioxidants, terpenes, flavenoids, and other phytochemicals extracted from OO that contribute to its unique chemical composition (Wolfrom et al., 1964; Da Costa et al., 1999; Djapiæ et al., 2003). These chemicals are responsible for OO wood being resistive to oxidative, bacterial and fungal decay as well as insect attacks, making it an ideal building material (especially for fence posts) (Clopton and Roberts, 1949; Smith and Perino, 1981; Monache et al., 1995).

PLA–OO composites offers interesting future commercial possibilities as agricultural mulch films because of its biodegradability, low cost fill (reducing PLA costs) and as a matrix for controlled release of phyto-active agents naturally occurring within Osage Orange wood. An active PLA–OO agricultural mulch film with beneficial and inherent chemical functions may offer an effective and economically feasible medium compared to inert petroleum-based plastics currently used in the fields.

2. Materials and methods

PLA was obtained from Dow Cargill (Minneapolis, MN) and contained over 90% L-lactide. The weight-average and number-average molecular weights were 148,000 and 110,000 respectively. The glass transition temperature (T_g) was 58 °C, and the melt temperature was 155 °C as determined by differential scanning calorimetry (DSC).

Osage Orange wood was harvested by chain saw removal of branches (diameter = ∼3–4 in.) from mature trees (est. 50 years old) in Brimfield, IL. Branches were stripped of leaves and then ground in a chipper/shredder (Model # CS410, Troy-Bilt, MTD, Cleveland, OH) equipped with 10 HP engine (Briggs and Stratton, Wauwatosa, WI). Ground chips were collected in a nylon sack and reintroduced through the chipper two additional times to reduce their size. Chips were processed in a Thomas-Wiley mill grinder (Model 4, Thomas Scientific, Swedesboro, NJ) equipped with 6 stationary cutting knives within a grinding chamber (197 mm inside diameter × 76 mm deep) rotated at 800 rpm. Wood particles exited through a 2 mm diameter stainless steel screen and were collected into a 1.8 l Mason glass jar. Particles were then sized through a Ro-Tap® Shaker (Model RX-29, Tyler, Mentor, OH) employing 203 mm diameter stainless steel screens. Sieve/Screens employed were #40, #50, #80, #140, and #200 US Standards (Newark Wire Cloth Company, Clifton, NJ). The shaker was operated for 60 min intervals at 278 rpm to obtain particle separation. Each screen fraction was then removed and oven dried for 48 h at 50 °C. In this work, the particle size of the OO is inversely related to the screen size thus the #50 screen has the largest particles and the #200 screen has the finest particles.

PLA and dried OO wood (10% or 25%, w/w) were thoroughly mixed using an industrial mixer (Kitchen Aid) and extruded at reduced moisture (less than 1%). Ribbons were prepared with a single-screw extruder (C.W. Brabender, South Hackensack, NJ) with four temperature zones (150, 170, 170, and 150 °C). A 3:1 high shear mixing zone screw was employed with a hangar-type die at 150 °C.

Ribbons were cut into ASTM D638-99 Type V tensile bars (6.0 cm × 1.0 cm) and evaluated using a mechanical property testing machine (Model 1122, Instron Corporation, Norwood, MA). The thickness was measured with a micrometer (Ames, Waltham, MA). Initial samples (dry) were conditioned for approximately 48 h at standard room temperature and humidity (23 °C and 50% RH). Wet samples were conditioned for 600 h under a 95% RH environment and periodically weighed to determine moisture uptake.

Thermal analysis to determine degree of crystallinity of the PLA matrix was conducted by DSC. A dual-cell differential scanning calorimeter (PerkinElmer DSC 7, Newark, CT) with Pyris Series software was used. The sample (approximately 20 mg) was placed in a stainless steel pan. The scan range was 20–180 °C with a rate of 10 °C/min.

PLA with 10% and 25% OO composite samples of 0.1 g were incubated at 25 °C in 10 ml of water, dichloromethane or methanol for 24 h. Absorbance readings were conducted on 2 ml aliquot samples with a UV/Visible spectrophotometer (UV-1601PC, Shimadzu Inc., Kyoto, Japan) in the spectrophotometric wavelength range of 240–800 nm. Absorbance readings of 325 nm were compared.

3. Results and discussion

OO wood fractions were separated using a manual screen that provided only nominal particle sizes. For example, OO wood particles that did not pass through a #50 sieve were between 0.1 and 0.5 mm in size (Fig. 1a). OO wood particles that passed through the #200 sieve (fines) were significantly smaller (Fig. 1b). In this report, the particle size increases with decreasing screen number (i.e. #50 has the largest particles). Data is presented using screen size rather than particle size due to the variable aspect ratio (length, width, and diameter) of the wood particles and the irregularity of surface area. The plotted data in the figures have the smallest particles or "fines" arbitrarily designated as #400 for clarity. PLA and various OO particle sizes readily combined using extrusion, an industrial-scale thermomechanical process, to produce ribbons. SEM micrographs show that the OO particles were uniformly distributed in the PLA matrix (Fig. 2).

PLA–OO composites were exposed to 95% relative humidity atmosphere in order to determine the water uptake of the OO wood encapsulated by the hydrophobic polymer. Although the samples may be directly exposed to liquid water in a field application, they were not immersed in water to prevent the loss of water-soluble compounds and to inhibit hydrolytic degradation of the PLA. The samples were periodically weighed until the weight gain was sustained and appeared to reach equilibrium. Fig. 3 shows the water uptake for 10% and 25% (w/w) OO filled PLA. PLA is hydrophobic and does not absorb water beyond its ambient condition of 0.5%. PLA filled with 10% OO gained about 1% water and 25% OO gained around 4% water after 600 h of exposure. Stark (2001), working with pine wood flour (WF) at #40 and polypropylene (PP), showed a similar water uptake at 20% fill over 1000 h even when immersed in water (Stark, 2001). At lower fill, the mesh size did not play a significant role in moisture uptake. However, at 25% OO, the particle size seemed to have more of an effect on water uptake which could be the result of the aspect ratio of the particles disturbing the PLA matrix allowing more water to diffuse along the interfacial areas. The proposed system of using PLA–OO as an active agricultural enhancement for plant growth, weed and pest control, and reduction of soil erosion requires the composite film to be stable/durable in wet conditions but also allow the release of
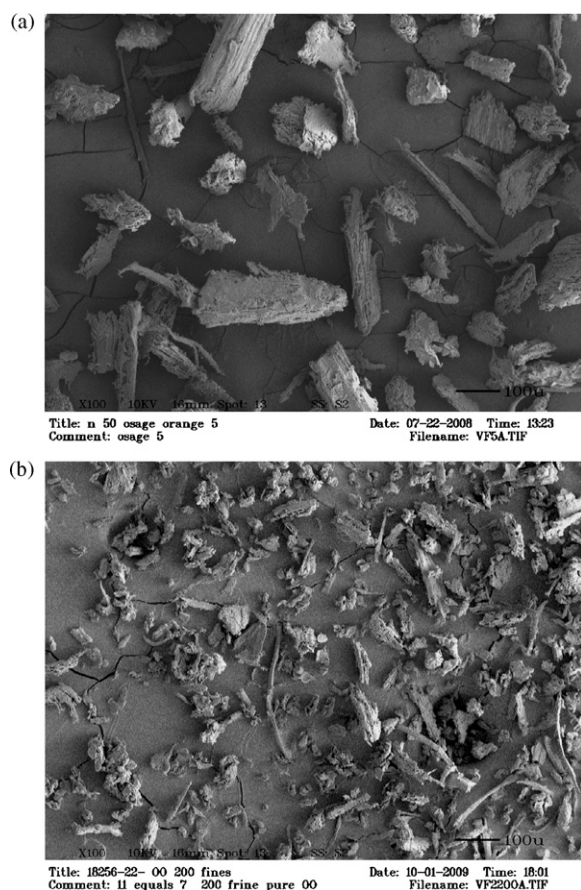
Fig. 1. SEM image of (a) #50 and (b) #200 OO fiber showing variation in aspect ratio. Irregularly shaped particles vary in size. Magnification is 100×.

Fig. 2. SEM images of (a) #50 and (b) #200 OO at 25% fill in PLA. Magnification is 500×.

the chemical compounds of OO into the environment. If PLA was completely hydrophobic, the bulk of the OO would be completely encapsulated and the release kinetics would be solely dependent on diffusion through the PLA until the PLA started to degrade 60–90 days after application. The ability to absorb some water is desirable to facilitate the release of the phytochemical compounds from OO into the environment.

The mechanical properties of PLA–OO composites were evaluated initially and after 600 h of exposure to a high humidity environment. The strength of a composite depends on the strength of each phase (PLA, OO) and the interfacial adhesion where stress transfer may occur. Tensile strength is shown in Fig. 4. The PLA control samples (wet and dry) show typical variation in tensile strength. On average, the 25% OO absorbed about 2–3% more water than the 10% OO, and the "dry" PLA–OO appears to retain more tensile strength than "wet" PLA–OO. The trend reported for PP–WF at 20% fill was that no significant differences in tensile strength occurred between wet and dry composites (Stark, 2001). This suggested that the contribution of PLA to the overall strength of the composite is less than that of PP. The decrease in tensile strength of PLA–OO is typical for filled PLA systems using cellulose fiber (Bourmaud and Pimbert, 2008), cellulosic wood fiber (Huda et al., 2005), lignin–cellulose (Hou et al., 2006), sugar beet pulp (Finkenstadt et al., 2007b), and oilseed lignocellulose (Finkenstadt et al., 2007a). At the same OO content, smaller particles retain more tensile strength than larger particles. Examining Fig. 2 shows that the PLA matrix is more continuous with smaller particles than larger particles, thus the tensile force is more evenly distributed. Larger particles contribute to more and larger defects in the polymer matrix resulting in loss of tensile strength. Young's modulus,
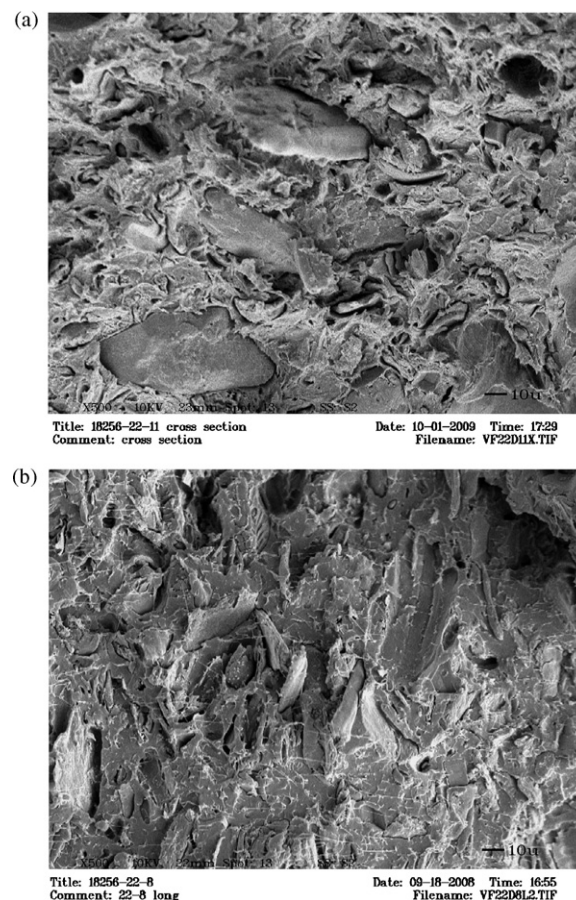
a measure of stiffness, shows no significant difference between the wet and dry PLA control. The modulus of PLA–OO with either 10% or 25% fill with very fine (#400) OO particles remains very close to the control values. The differences in modulus for OO particle size are readily seen in Fig. 5. Samples with 25% OO exhibited higher modulus than 10% OO as expected for a polymer composite. Wet samples generally had lower modulus indicating a softer composite although the 10% OO was not as sensitive to moisture. In general, these results were expected with a polymer composite filled with soft, wet wood and were similar to reported results (Huda et al., 2005; Bourmaud and Pimbert, 2008). Elongation, the amount the
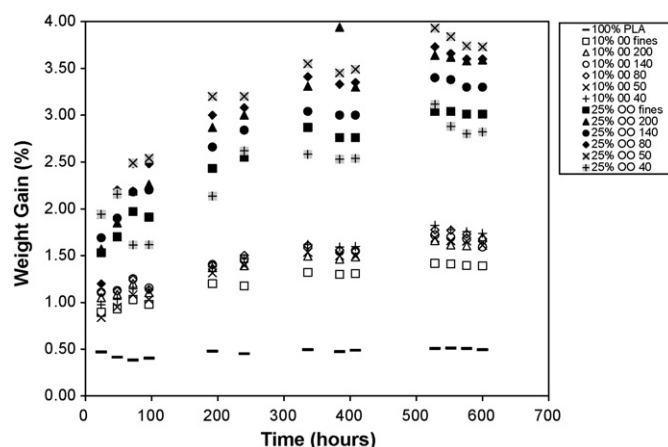

Fig. 3. Moisture uptake of PLA–OO composites at 95% RH over 600 h.
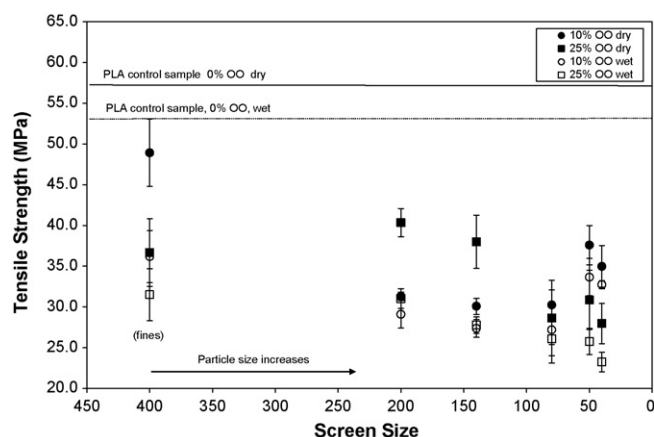
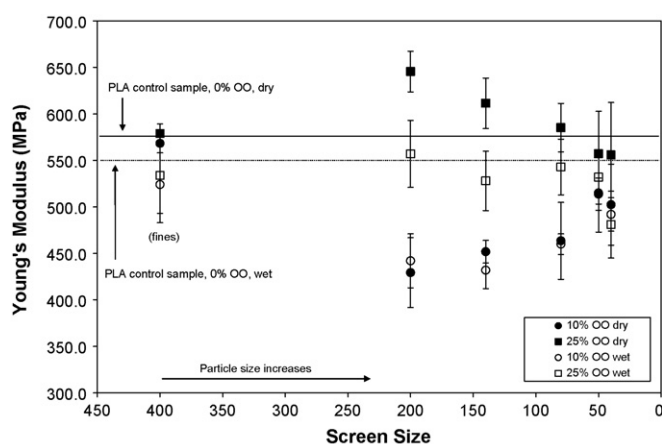Fig. 4. Tensile strength of PLA–OO composites in dry and wet conditions.

Fig. 5. Young's Modulus of PLA–OO composites in dry and wet conditions.

composite stretches before breaking, decreased with decreasing screen size and increasing particle size (Fig. 6). With fine particles (#400), the 10% OO exhibited greater elongation than its dry component or 25% OO. Wet composites exhibited slight increases in elongation.

The glass transition of every sample, regardless of OO content, was approximately 55 °C. The melting temperature was approximately 155 °C. However, the crystallinity of the PLA–OO was significantly higher for the 25% OO than the 10% OO (Fig. 7). Crys-
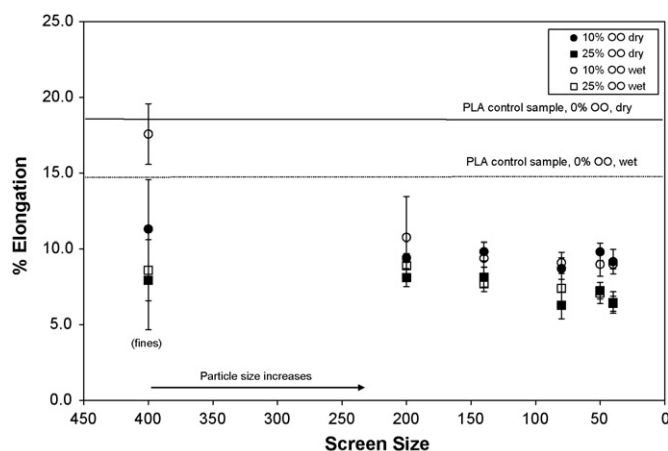

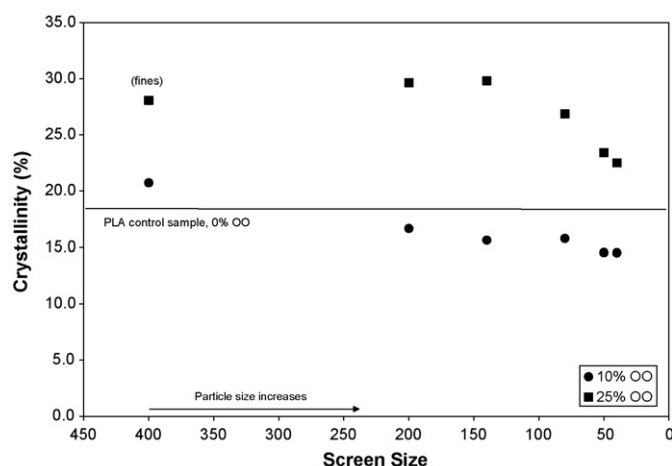Fig. 6. Elongation of PLA–OO composites in dry and wet conditions.

Fig. 7. Crystallinity of PLA–OO composites at 10% and 25% OO fill.

tallinity (%X) was calculated using the change in enthalpy and compensating for the filler (W_{pla}) using $\%X = 100 \times \Delta H / 93.7 \times W_{pla}$. The value of a PLA crystal is 97.3. Using wood fiber, Pilla et al. (2008) suggested the fiber acts as a nucleating agent and reported that PLA filled with 20% pine WF exhibited crystallinity of 38% while the control PLA was approximately 13% (Pilla et al., 2008). The PLA crystallinity reported in this work was approximately 18%. Crystallinity with 25% OO increased to around 27% with the finest particles and steadily decreased as particle size increased. At 10% fill, there was no significant difference in crystallinity between PLA–OO and the PLA control.

Osage Orange wood contains several phenolics including flavonols, flavanones, xanthones (Wolfrom et al., 1964; Da Costa et al., 1999) and stilbenes (e.g., oxyresveratrol) (Djapiæ et al., 2003). Initial results indicated that the thermomechanical treatment during compounding of PLA–OO composites resulted in higher release of organic compounds than from non-thermal solution cast composites. The ultraviolet spectra of OO root bark phenolics and pigments (e.g., xanthones) express themselves in the region between 230 and 340 nm (Wolfrom et al., 1964). Xanthones have been identified as macluraxanthone, osajaxanthone, and alvaxanthone triacetate and are responsible for the yellow color characteristic of OO. The wavelength, 325 nm, was selected as a compromise spectrophotometic reading to monitor the occurrence and release of phenolics from PLA–OO composites. There was a strong positive correlation between OO fraction size and percent composition and absorbance readings. Proportionally higher absorbance readings were obtained with 25% PLA–OO than 10% PLA–OO, regardless of the particle size. Administration of dichloromethane to PLA or PLA–OO composites resulted in the complete liquidation (degradation) of the polymeric material in 24 h. Treatment with methanol resulted in about a 25% degradation of the PLA and PLA–OO materials in 24 h. This is reflected in the absorbance readings taken at 325 nm. Lowest absorbance readings occurred in #40 PLA–OO while highest absorbance readings were occurred in #200 and "fine" (#400) PLA–OO fractions. For example, methanol absorbance readings increased 154% employing PLA–OO with #200 wood compared to readings conducted with PLA–OO with #40 indicating that the xanthones were more readily available and released from smaller particles. Depending on the sieved wood fraction employed, dichloromethane readings were consistently higher (2–4×) than methanol readings. These observations were attributed to a correlation with the degree of degradation of the PLA by the solvents employed.

4. Conclusion

Future work will include investigating the degradation of PLA–OO by accelerated chemical means and composting conditions as well as evaluation of soil conditions and plant growth in composted PLA–OO media. The mechanical properties of PLA–OO composites were evaluated in dry and wet conditions. Higher concentration and larger particle sizes of OO generally had a greater effect on the mechanical properties especially the modulus. Crystallinity of the PLA was significantly higher at 25% OO fill corresponding to a smaller continuous polymer phase. In addition, the organic compounds of OO are readily available for release into the environment. PLA–OO composites can be used as agricultural mulch films with several advantages over existing products including biodegradability, growth promotion and controlled release of organic compounds.

Acknowledgements

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